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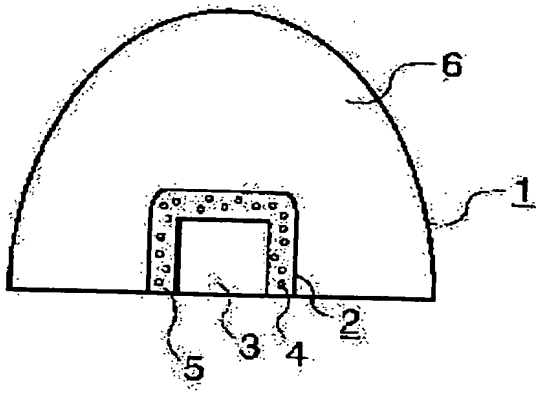
(54) LIGHT EMITTING ELEMENT

(57)Abstract:
PROBLEM TO BE SOLVED: To improve the lifetime of a light emitting element.
SOLUTION: The light emitting element 1 is provided with a light emitting diode 3 and a fluorescence layer 2. In order to improve the lifetime of the light emitting element 1, fluorescent substance 4 of the fluorescence layer 2 is provided with water-resistant coating.



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CLAIMS

[Claim(s)]
[Claim 1] The light emitting device to which at least one light emitting diode and a fluorescence layer are prepared, and this fluorescent substance is characterized by having at least one fluorescent substance which has coating.
[Claim 2] The light emitting device according to claim 1 characterized by choosing said coating from the group which consists of an organic material, an inorganic material, and a glass ingredient.
[Claim 3] The light emitting device according to claim 2 characterized by choosing said organic material from the group which consists of a latex and polyorganosiloxane.
[Claim 4] The light emitting device according to claim 2 characterized by choosing said glass ingredient from the group which consists of a borosilicate, a phospho silicate, and an alkali silicate.
[Claim 5] The light emitting device according to claim 2 characterized by choosing said inorganic material from the group which consists of combination of an oxide, a borate, phosphate, and these ingredients.
[Claim 6] The light emitting device according to claim 5 characterized by considering as the orthophosphate MPO4 which chose said phosphate from the group which consists M of aluminum, La, Sc, Y, and Lu, or the polyphosphate which has the presentation (M0.5PO3) which chose the chain length n and M between 101 and 106 from calcium, Sr, and Ba.
[Claim 7] The light emitting device according to claim 1 characterized by choosing said illuminant from the group which consists of an oxidization illuminant, a sulfuration illuminant, an ulmin acid illuminant, a boric-acid illuminant, a vanadium illuminant, and a silicic-acid illuminant.
[Claim 8] said ulmin acid emitter — Y3aluminum5O12:Ce, 3(Y, Gd) (aluminum, Ga)5O12:Ce, and BaMgAl10O17: — the light emitting device according to claim 7 characterized by choosing from the group which consists of Eu and Mn.
[Claim 9] The light emitting device according to claim 7 characterized by choosing said sulfuration emitter from SrS:Eu, SrGa2 S4:Eu, 2 (aluminum (Sr, calcium, Ba), Ga) S4:Eu, SrY2 S4:Eu, S:Eu (Mg, calcium), SrS:Ce, CaS:Ce, CaLa2 S4:Ce and CaS:Ce, and the group that consists of Eu.
[Claim 10] A light emitting device given in any 1 term of the claims 1-9 characterized by said light emitting device containing SrS:Eu which has coating of SiO2 and a silicate.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the light emitting device which prepared at least one light emitting diode and a fluorescence layer.
[0002]
[Description of the Prior Art] The solid-state light source, for example, light emitting diode, especially semiconductor diode are known conventionally. Luminescence of semiconductor diode is based on the recombination of an electronic-hole pair (exciton) of the transition region of pn transition of the semi-conductor which was able to apply bias to the forward direction. The dimension of the band gap of a semi-conductor determines the wavelength of the emitted light roughly.
[0003] The semiconductor diode which emits the light is used also with a color display. In a color display, red, green, and blue in three primary colors are generated by the array of red luminescence semiconductor diode, green luminescence semiconductor diode, and blue luminescence semiconductor diode. However, the approach of attaining the color picture description near a genuine article, especially true description green [in an image] and blue in this case poses a problem.
[0004] By development of the semiconductor diode which performs UV radiation, the possibility of the true color picture display on the color picture screen which addresses diode is increasing. By combining the semiconductor diode which performs UV radiation, and the emitter which changes UV radiation into the light, the color and white of the arbitration of the lights of the request by semiconductor diode can be expressed. Such a color display is known from the Germany patent number No. 19800983. This principle is applied also to the semiconductor diode which carries out outgoing radiation of purple or the blue glow, when using a suitable emitter.
[0005]
[Problem(s) to be Solved by the Invention] The main advantages of the luminescence semiconductor diode at the time of comparing with the conventional lamp are the long lives accompanying high stability and high it. The limiting factor of the color picture screen which addresses diode is the stability of the fluorescent substance used in a fluorescence layer. Since a fluorescent substance is not thoroughly separated from a circumference ambient atmosphere, the fluorescent substance reacted to water has a possibility that the moisture from air may hydrolyze. A comparatively stable fluorescent substance also has a possibility of hydrolyzing under an elevated temperature and the effect of high humidity. The life of a light emitting device is shortened by degradation of the fluorescent substance in a fluorescence layer.
[0006] The object of this invention is offering the light emitting device whose life in which light emitting diode and a fluorescence layer were prepared improved.
[0007]
[Means for Solving the Problem] This object prepares at least one light emitting diode and a fluorescence layer, and it is attained by the light emitting device to which this fluorescent substance is characterized by having at least one fluorescent substance which has coating.
[0008] Degradation produced with the moisture in air is prevented by coating of the fluorescent substance particle which has the waterproof film of high density.
[0009] Suitably, said coating is chosen from the group which consists of an organic material, an inorganic material, and a glass ingredient.
[0010] Furthermore, said organic material is suitably chosen from the group which consists of a latex and polyorganosiloxane.
[0011] Furthermore, said glass ingredient is suitably chosen from the group which consists of a borosilicate, a phospho silicate, and an alkali silicate.
[0012] Furthermore, said inorganic material is suitably chosen from the group which consists of combination of an oxide, a borate, phosphate, and these ingredients.
[0013] It does not deteriorate by radiation which these organic materials, a glass ingredient, and an inorganic material form insoluble coating to water to a fluorescent substance particle by closing in, and the coating does not react with a fluorescent substance, and has the wavelength of UV radiation, i.e., 410 to 450 nm. Furthermore, coating is colorlessness, therefore does not affect the value of the color of a fluorescent substance.
[0014] A suitable example is characterized by considering as the orthophosphate MPO4 which chose said phosphate from the group which consists M of aluminum, La, Sc, Y, and Lu, or the polyphosphate which has the presentation

(M0.5PO3) which chose the chain length n and M between 101 and 106 from calcium, Sr, and Ba.
[0015] These phosphate forms the fully bolted thin film which has the front face of high density on a fluorescent substance.
[0016] Suitably, said illuminant is chosen from the group which consists of an oxidization illuminant, a sulfuration illuminant, an ulmin acid illuminant, a boric-acid illuminant, a vanadium illuminant, and a silicic-acid illuminant.
[0017] By combining these emitters with a suitable activator, UV radiation or blue glow is further changed into the light of long wave length.
[0018] suitable — said ulmin acid emitter — Y3aluminum5O12:Ce, 3(Y, Gd) (aluminum, Ga)5O12:Ce, and BaMgAl10O17: — it chooses from the group which consists of Eu and Mn.
[0019] If especially Y3aluminum 5O12 that has special coating is excited by blue glow, it will serve as a fluorescent substance which emits yellow.
[0020] Furthermore, said sulfuration emitter is suitably chosen from SrS:Eu, SrGa2 S4:Eu, 2 (aluminum (Sr, calcium, Ba), Ga) S4:Eu, SrY2 S4:Eu, S:Eu (Mg, calcium), SrS:Ce, CaS:Ce, CaLa2 S4:Ce and CaS:Ce, and the group that consists of Eu.
[0021] Especially the fluorescent substance containing a sulfide like SrS:Eu is hydrolyzed by the moisture in air based on the following reaction formulae.
A fluorescent substance is stabilized by SrS+2H2 O->Sr(OH)2+H2S, therefore coating which has a sulfide suitably.
[0022] Furthermore, said light emitting device contains suitably SrS:Eu which has coating of SiO2 and a silicate.
[0023]
[Embodiment of the Invention] As shown in drawing 1 , a light emitting device 1 is equipped with the diode 2 which emits UV radiation or blue glow when the easiest, and the fluorescence layer 2 prepared in diode 3. The fluorescence layer 2 is equipped with the clear layer 5 which has the fluorescent substance 4 which performed waterproof coating with the gestalt of this operation. The ingredient of a clear layer 5 can be used as polyacrylate (polyacrylate), polystyrol (polystyrol), an epoxy resin (epoxide resin), polypropylene, a polycarbonate, or some [other] polymers.
[0024] A light emitting device 1 like the product mass-produced is usually protected by the epoxy housing 6 with which the lens of an epoxy resin is fabricated. This lens plays the role which raises advice of the light from a light emitting device 1. With the gestalt of this operation, the fluorescence layer 2 may be formed between a clear layer 5 and the epoxy housing 6. The fluorescence layer 2 can also be formed as coating of the outside of the epoxy housing 6. The fluorescence layer 2 contains fluorescent substance mixture (phosphor) equipped with the fluorescent substance 4 which prepared coating in these cases. With the gestalt of other operations, the fluorescence layer 2 is formed from an epoxy resin, and coating is prepared in a fluorescent substance 4. With the gestalt of this operation, the fluorescence layer 2 forms the epoxy housing 6.
[0025] When a light emitting device should carry out outgoing radiation of the white light, a fluorescence layer includes physical mixing of the fluorescent substance which emits the fluorescent substance which emits red, the fluorescent substance which emits blue, and green.
[0026] A large-sized two-dimensional display can be easily manufactured by the array of light emitting diode 3. The array of such light emitting diode 3 can be covered with the glass plate against which it was pushed by the fluorescence layer 2. The fluorescence layer 2 is equipped with the red emitter, green emitter, and blue emitter which were prepared by the three-point pattern arranged to the triangle.
[0027] The diode 3 which carries out outgoing radiation of the UV contains INGaN or GaN. The diode 3 which carries out outgoing radiation of this UV has the maximum luminescence between 370nm which is half-value-width FWHM<50nm, and 410nm (emission maximun). The diode 3 which carries out outgoing radiation of the blue glow which has the wavelength between 410nm and 450nm has for example, InGaN/AlGaN structure. A means to supply electric energy to the diode 3 which carries out outgoing radiation of UV or the blue glow is established in order to maintain luminescence. The means has at least two electrodes.
[0028] Let the fluorescent substance used in the fluorescence layer 2 be for example, an oxidization fluorescent substance, a sulfuration fluorescent substance, an ulmin acid fluorescent substance, a way acid fluorescent substance, a vanadium acid fluorescent substance, or a silicic acid fluorescent substance.
Especially :Y3aluminum5O12:Ce for which the following fluorescent substances are used, 3 (Y, Gd) 5O12: (aluminum, Ga) Ce, BaMgAl10O17: It Eu(s). Eu, Mn, Y2O2 S:Eu, Bi, and YVO4: — Eu, Bi, and YVO4: — Eu, Bi, and YBO3: — Ce, Tb, 2(Sr, Ba) SiO4:Eu, calcium2MgSi2O7:Eu, Sr2CeO4:Eu, SrS:Eu, and SrGa2S4: — (Sr, calcium, Ba) 2 S4:Eu, SrY2 S4:Eu, S:Eu (calcium, Sr), S:Eu (Mg, calcium), SrS:Ce, CaS:Ce, CaLa2 S4:Ce or CaS:Ce, Eu (aluminum, Ga).
[0029] The particle of a fluorescent substance 4 is covered in a flat waterproof layer by closing in. a logarithm — the thickness of the layer of coating is usually 0.001 to 0.2 micrometer, therefore since it is dramatically thin, a photon can pass a layer, without losing most energy.
[0030] Formation of coating follows various approaches according to a coating ingredient.
[0031] In order to cover a fluorescent substance with a latex, a latex is dissolved with an organic solvent. Then, a fluorescent substance 4 suspends in this solvent (suspend). A latex precipitates to the particle of a fluorescent substance 2 by adding the solvent which a latex does not dissolve (precipitate). After filtering and drying the fluorescent substance by which coating was carried out, melting (fuse) of the latex is carried out at an elevated temperature.
[0032] Coating containing a polysiloxane is obtained by mixing a polysiloxane directly to a fluorescent substance 4. A polysiloxane can be fused to an organic solvent and this solvent can also be made to suspend a fluorescent

substance 4 after that instead. Cross linking of the polysiloxane pasted up on the particle of a fluorescent substance.4 is carried out by overheating, the catalyst, or radical initiation (radicalinitiation) after evaporation of a solvent.

[0033] In order to manufacture glass type coating from a borosilicate, a phospho silicate (phosphosilicate), or an alkali silicate, the colloidal solution of the silicate of a potassium silicate or a specific silicate is added to an ammonium hydroxide solvent. After adding a fluorescent substance 4, the mixture obtained as a result is stirred powerfully. While filtering and taking out the fluorescent substance 4 which has coating, it dries at 100 degrees C.

[0034] It is advantageous to coating that SiO2 is included [in a predetermined case] in addition to silicate. In order to manufacture such coating, the colloidal solution of a borosilicate, a phospho silicate, or an alkali silicate is added to an ammonium hydroxide solution. After adding a fluorescent substance 4, the solution of the tetraethyl orthosilicic acid salt in ethanol (tetraethyl orthosilicate) is added to mixture, and the mixture obtained as a result is stirred powerfully. The fluorescent substance 4 which has coating is dried at 100 degrees C while it is taken out.

[0035] In order to increase stability, the 2nd coating layer can be prepared. For this reason, as already explained, the colloidal solution of a borosilicate, a phospho silicate, or an alkali silicate is added to an ammonium hydroxide solution. First, the fluorescent substance 4 which already prepared coating is added to this mixture, and the solution of the tetraethyl orthosilicic acid salt in ethanol (tetraethyl orthosilicate) is added after that. After stirring powerfully, while taking out the fluorescent substance 4 which carried out duplex coating, it dries at 100 degrees C.

[0036] In order to form coating of an inorganic material, suspension including the combination of a desired coating ingredient, for example, oxide, a borate, phosphate, or these coatings ingredient is made.

[0037] It is converted into instead of by the desired particle by heat treatment after that also including the precursor of the coating ingredient according [suspension] to this invention. First, the suspension which follows, for example, contains Mg (OH)2 is prepared on the particle of a fluorescent substance 4, and is thermally converted into the layer of MgO after that.

[0038] Let especially the initiation compound used for coating containing MgO, aluminum2O3, and oxide like SiO2 be a water-soluble metal salt, a water-soluble nitrate, acetate, or citrate. One or more of the metal salts of these are underwater dissolved, while making a coating solution, and a pH value is adjusted to 7. The fluorescent substance 4 which should be covered is diffused in this solution. Thus, the aqueous suspension of the obtained fluorescent substance 4 continues contacting the ambient atmosphere which contains ammonia with scrambling until an oxide or a hydroxide precipitates to a fluorescent substance particle, while the pH value of suspension rises to 9.5. The fluorescent substance 4 which has coating is removed, and it dries. When a fluorescent substance is covered with a hydroxide, it is calcinated at the temperature which rises gradually and is converted into the oxide with which a hydroxide corresponds.

[0039] In order to cover a fluorescent substance 4 with SiO2, it prepares first suitably, the silicic acid anhydride which can be hydrolyzed, for example, the tetraethyl orthosilicic acid, of a monomer. After adding a fluorescent substance 4, the mixture obtained as a result is stirred powerfully, and a solvent, for example, ethanol, is removed after that. The fluorescent substance 4 which has coating is exposed to the ambient atmosphere saturated with a 80-degree C steam in order to obtain coating of SiO2 of high density.

[0040] The silicic acid anhydride which can be hydrolyzed may beforehand already be condensed selectively. For this reason, it mixes in the amount of catalysts of Rarefaction HCl, and the silicic acid anhydride of a monomer is heated under reflux for 24 hours. Then, distillation removes, without including the silicic acid anhydride beforehand condensed in the solvent.

[0041] Let the initiation compound used to coating containing an orthophosphate be the fusibility metal salt which has presentation MX3 and H2O. In this case, M expresses one of Metals aluminum, Sc, Y, Lu, and La, X expresses one or more of anion CH3COO-, RO-, NO3-, Cl-, CH3COCH=C(O-) CH3, and -OOCCH2CH(OH) (COO-) CH2COO- , and y expresses the number more than zero. Generally as a solvent, water is used.

[0042] a phosphoric acid — a phosphoric acid and a urea are suitably added to this solution 85%. After filtering suitably the solution obtained as a result with a thin film nylon filter, a fluorescent substance 4 is added. It heats stirring suspension until the pH value is set to 7. After cooling to a room temperature, the fluorescent substance 4 which has coating 4 is taken out, rinsed and dried.

[0043] In order to form coating constituted from a polyphosphate, the water solution of a polyphosphate is added to the suspension of the fluorescent substance 4 which should be covered. A polyphosphate has presentation (M0.5PO3) n, and chooses M from the group of calcium, Sr, and Ba in this case, and chain length n is between 101 and 106. The water solution of the water-soluble salt of calcium, Sr, or Ba is added to this suspension. The pH value of suspension is held to an alkali field by adding ammonia or the caustic alkali solution of sodium. The fluorescent substance 4 which has coating is taken out, rinsed and dried.

[0044] In order to form coating constituted from way acid chloride, the suspension of the fluorescent substance 4 which should be covered is added to the alcoholic solution of way acid ester, and the ester is obtained from the multi-way acid (polyboric acid) which has general formula Hn-2BnO2n-1. In this case, it is n<=3. The reaction mixture obtained as a result is stirred at a room temperature for 2 to 24 hours, and the fluorescent substance 4 which has coating is taken out, and it is dried.

[0045] The example of this invention is explained to a detail below.

[0046] an example 1 — first — 30.0g (TEOS) of tetraethyl orthosilicic acid salts in 40.0ml dehydrated ethanol — 0.1M It mixes to HCl0.864ml. The reaction mixture obtained as a result is heated under reflux for 24 hours. Then, TEOS and ethanol to which condensation was not performed are removed by distillation.

[0047] SrS:Eu10g is suspended in 50.0ml of dehydrated ethanol. TEOS condensed beforehand is added to this suspension, and the mixture obtained as a result is stirred for 15 minutes. SrS:Eu which covered TEOS obtained as a result after distillation of the solvent in a vacuum is exposed to the air containing a steam with a temperature of 80 degrees C. Thickness of coating of SiO2 is set to 100nm.

[0048] A table 1 shows that quantum efficiency hardly decreases by coating of the fluorescent substance particle of SrS:Eu by the layer of SiO2 which has 100nm thickness.

[0049] Table 1: Quantum efficiency (Q. E.) of SrS:Eu which covered SiO2, and SrS:Eu, absorption (Abs.), and surface presentation [table 1]

	QE [%]	Abs. [%]	Sr [原子%]	S [原子%]	O [原子%]	Si [原子%]	C [原子%]
SrS:Eu	100	76.4	16.3	14.2	66.3	-	3.2
SiO_2-SrS:Eu	97	77.6	-	-	46.3	12.5	41.2

[0050] Next, the light emitting device 1 which has the fluorescence layer 2 containing SrS:Eu which covered the diode 3 which emits blue glow, and SiO2 is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further SrS:Eu which covered SiO2 as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.

[0051] Example 2 ammonia 250g is mixed in 750g of water, and 25g of potassium-silicate solutions of colloid (15 % of the weight) is added to this mixture. Then, SrS:Eu is added and the suspension obtained as a result is stirred powerfully. The solution of 10ml of tetraethyl orthosilicic acid salts of ethanol 750ml Naka is dropped at suspension for the period for less than 15 minutes. The reaction mixture obtained as a result is stirred for 90 minutes at a room temperature. Covered SrS:Eu is taken out and it dries at 100 degrees C. The covered fluorescent substance is again suspended in the mixture of 25g of potassium silicates on ammonia 250g in 750g of water, and colloid. 1l. of ethanol, and ethanol 500ml -- 10ml [of inner tetraethyl orthosilicic acid] mixture is dropped at this suspension. The reaction mixture obtained as a result is stirred for 60 minutes at a room temperature. SrS:Eu which has coating of a potassium silicate is taken out and it dries at 100 degrees C.

[0052] Subsequently, the light emitting device 1 which has the fluorescence layer 2 containing SrS:Eu which covered the diode 3 and the potassium silicate which emit blue glow is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. If a fluorescent substance 4 is formed on a clear layer 5, the fluorescence layer 2 containing SrS:Eu which covered the potassium silicate will be formed. Then, a light emitting device 1 is protected by the epoxy housing 6.

[0053] Example 3aluminum(NO3)3.9H2O4.45g is dissolved into 1.25l. of pure water. 85%H3PO41.37g and 36.04g of ureas are added to this solution. SrGa2 S4 is added after filtering the mixture obtained as a result in the nylon filter of 0.2 micrometers of thickness. Suspension is stirred at 90 degrees C until the pH value of a solution is set to 7. Suspension can be cooled to a room temperature, and ejection and pure water wash fluorescent substance SrGa2 S4 which covered AlPO4 several times, and it heats at 100 degrees C for 1 hour.

[0054] Subsequently, the light emitting device 1 which has the fluorescence layer 2 containing SrGa 2O4 which covered the diode 3 and AlPO4 which emit blue glow is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further SrGa2 S4 which covered AlPO4 as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.

[0055] Example 4(3.9 mols) Mg(NO3)2.6H2O1.0g is dissolved into 50ml of water. Y3aluminum 5O12 is suspended in 50ml of water, and a magnesium nitride solution is added to this suspension. The suspension which has the pH value of 7.5 and which was obtained as a result is stirred powerfully. The pH value of suspension rises to pH9.1 with concentration ammonia liquor, consequently Mg (OH)2 begins to precipitate. After stirring powerfully for 2 hours, the fluorescent substance with which coating was performed is taken out, and it dries at 80 degrees C, and is eventually calcinated at 250 degrees C for 2 hours.

[0056] The light emitting device 1 which has the fluorescence layer 2 containing Y3aluminum 5O12 which covered the diode 3 which emits blue glow, and MgO is manufactured. For this reason, for this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further Y3aluminum 5O12 which covered MgO as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the light emitting device which prepared at least one light emitting diode and a fluorescence layer.

[Translation done.]

PRIOR ART

[Description of the Prior Art] The solid-state light source, for example, light emitting diode, especially semiconductor diode are known conventionally. Luminescence of semiconductor diode is based on the recombination of an electronic-hole pair (exciton) of the transition region of pn transition of the semi-conductor which was able to apply bias to the forward direction. The dimension of the band gap of a semi-conductor determines the wavelength of the emitted light roughly.

[0003] The semiconductor diode which emits the light is used also with a color display. In a color display, red, green, and blue in three primary colors are generated by the array of red luminescence semiconductor diode, green luminescence semiconductor diode, and blue luminescence semiconductor diode. However, the approach of attaining the color picture description near a genuine article, especially true description green [in an image] and blue in this case poses a problem.

[0004] By development of the semiconductor diode which performs UV radiation, the possibility of the true color picture display on the color picture screen which addresses diode is increasing. By combining the semiconductor diode which performs UV radiation, and the emitter which changes UV radiation into the light, the color and white of the arbitration of the lights of the request by semiconductor diode can be expressed. Such a color display is known from the Germany patent number No. 19800983. This principle is applied also to the semiconductor diode which carries out outgoing radiation of purple or the blue glow, when using a suitable emitter.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The main advantages of the luminescence semiconductor diode at the time of comparing with the conventional lamp are the long lives accompanying high stability and high it. The limiting factor of the color picture screen which addresses diode is the stability of the fluorescent substance used in a fluorescence layer. Since a fluorescent substance is not thoroughly separated from a circumference ambient atmosphere, the fluorescent substance reacted to water has a possibility that the moisture from air may hydrolyze. A comparatively stable fluorescent substance also has a possibility of hydrolyzing under an elevated temperature and the effect of high humidity. The life of a light emitting device is shortened by degradation of the fluorescent substance in a fluorescence layer.
[0006] The object of this invention is offering the light emitting device whose life in which light emitting diode and a fluorescence layer were prepared improved.

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* NOTICES *

MEANS

[Means for Solving the Problem] This object prepares at least one light emitting diode and a fluorescence layer, and it is attained by the light emitting device to which this fluorescent substance is characterized by having at least one fluorescent substance which has coating.
[0008] Degradation produced with the moisture in air is prevented by coating of the fluorescent substance particle which has the waterproof film of high density.
[0009] Suitably, said coating is chosen from the group which consists of an organic material, an inorganic material, and a glass ingredient.
[0010] Furthermore, said organic material is suitably chosen from the group which consists of a latex and polyorganosiloxane.
[0011] Furthermore, said glass ingredient is suitably chosen from the group which consists of a borosilicate, a phospho silicate, and an alkali silicate.
[0012] Furthermore, said inorganic material is suitably chosen from the group which consists of combination of an oxide, a borate, phosphate, and these ingredients.
[0013] It does not deteriorate by radiation which these organic materials, a glass ingredient, and an inorganic material form insoluble coating to water to a fluorescent substance particle by closing in, and the coating does not react with a fluorescent substance, and has the wavelength of UV radiation, i.e., 410 to 450 nm. Furthermore, coating is colorlessness, therefore does not affect the value of the color of a fluorescent substance.
[0014] A suitable example is characterized by considering as the orthophosphate MPO4 which chose said phosphate from the group which consists M of aluminum, La, Sc, Y, and Lu, or the polyphosphate which has the presentation (M0.5PO3) which chose the chain length n and M between 101 and 106 from calcium, Sr, and Ba.
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[0016] Suitably, said illuminant is chosen from the group which consists of an oxidization illuminant, a sulfuration illuminant, an ulmin acid illuminant, a boric-acid illuminant, a vanadium illuminant, and a silicic-acid illuminant.
[0017] By combining these emitters with a suitable activator, UV radiation or blue glow is further changed into the light of long wave length.
[0018] suitable -- said ulmin acid emitter -- Y3aluminum5O12:Ce, 3(Y, Gd) (aluminum, Ga)5O12:Ce, and BaMgAl10O17: -- it chooses from the group which consists of Eu and Mn.
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[0020] Furthermore, said sulfuration emitter is suitably chosen from SrS:Eu, SrGa2 S4:Eu, 2 (aluminum (Sr, calcium, Ba), Ga) S4:Eu, SrY2 S4:Eu, S:Eu (Mg, calcium), SrS:Ce, CaS:Ce, CaLa2 S4:Ce and CaS:Ce, and the group that consists of Eu.
[0021] Especially the fluorescent substance containing a sulfide like SrS:Eu is hydrolyzed by the moisture in air based on the following reaction formulae.
A fluorescent substance is stabilized by SrS+2H2 O->Sr(OH)2+H2S, therefore coating which has a sulfide suitably.
[0022] Furthermore, said light emitting device contains suitably SrS:Eu which has coating of SiO2 and a silicate.
[0023]
[Embodiment of the Invention] As shown in drawing 1 , a light emitting device 1 is equipped with the diode 2 which emits UV radiation or blue glow when the easiest, and the fluorescence layer 2 prepared in diode 3. The fluorescence layer 2 is equipped with the clear layer 5 which has the fluorescent substance 4 which performed waterproof coating with the gestalt of this operation. The ingredient of a clear layer 5 can be used as polyacrylate (polyacrylate), polystyrol (polystyrol), an epoxy resin (epoxide resin), polypropylene, a polycarbonate, or some [other] polymers.
[0024] A light emitting device 1 like the product mass-produced is usually protected by the epoxy housing 6 with which the lens of an epoxy resin is fabricated. This lens plays the role which raises advice of the light from a light emitting device 1. With the gestalt of this operation, the fluorescence layer 2 may be formed between a clear layer 5 and the epoxy housing 6. The fluorescence layer 2 can also be formed as coating of the outside of the epoxy housing 6. The fluorescence layer 2 contains fluorescent substance mixture (phosphor) equipped with the fluorescent substance 4 which prepared coating in these cases. With the gestalt of other operations, the fluorescence layer 2 is formed from an epoxy resin, and coating is prepared in a fluorescent substance 4. With the gestalt of this operation, the fluorescence layer 2 forms the epoxy housing 6.

[0025] When a light emitting device should carry out outgoing radiation of the white light, a fluorescence layer includes physical mixing of the fluorescent substance which emits the fluorescent substance which emits red, the fluorescent substance which emits blue, and green.
[0026] A large-sized two-dimensional display can be easily manufactured by the array of light emitting diode 3. The array of such light emitting diode 3 can be covered with the glass plate against which it was pushed by the fluorescence layer 2. The fluorescence layer 2 is equipped with the red emitter, green emitter, and blue emitter which were prepared by the three-point pattern arranged to the triangle.
[0027] The diode 3 which carries out outgoing radiation of the UV contains INGaN or GaN. The diode 3 which carries out outgoing radiation of this UV has the maximum luminescence between 370nm which is half-value-width FWHM<50nm, and 410nm (emission maximun). The diode 3 which carries out outgoing radiation of the blue glow which has the wavelength between 410nm and 450nm has for example, InGaN/AlGaN structure. A means to supply electric energy to the diode 3 which carries out outgoing radiation of UV or the blue glow is established in order to maintain luminescence. The means has at least two electrodes.
[0028] Let the fluorescent substance used in the fluorescence layer 2 be for example, an oxidization fluorescent substance, a sulfuration fluorescent substance, an ulmin acid fluorescent substance, a way acid fluorescent substance, a vanadium acid fluorescent substance, or a silicic acid fluorescent substance.
Especially :Y3aluminum5O12:Ce for which the following fluorescent substances are used, 3 (Y, Gd) 5O12: (aluminum, Ga) Ce, BaMgAl10O17: It Eu(s). Eu, Mn, Y2O2 S:Eu, Bi, and YVO4: — Eu, Bi, and YVO4: — Eu, Bi, and YBO3: — Ce, Tb, 2(Sr, Ba) SiO4:Eu, calcium2MgSi2O7:Eu, Sr2CeO4:Eu, SrS:Eu, and SrGa2S4: — (Sr, calcium, Ba) 2 S4:Eu, SrY2 S4:Eu, S:Eu (calcium, Sr), S:Eu (Mg, calcium), SrS:Ce, CaS:Ce, CaLa2 S4:Ce or CaS:Ce, Eu (aluminum, Ga).
[0029] The particle of a fluorescent substance 4 is covered in a flat waterproof layer by closing in. a logarithm — the thickness of the layer of coating is usually 0.001 to 0.2 micrometer, therefore since it is dramatically thin, a photon can pass a layer, without losing most energy.
[0030] Formation of coating follows various approaches according to a coating ingredient.
[0031] In order to cover a fluorescent substance with a latex, a latex is dissolved with an organic solvent. Then, a fluorescent substance 4 suspends in this solvent (suspend). A latex precipitates to the particle of a fluorescent substance 2 by adding the solvent which a latex does not dissolve (precipitate). After filtering and drying the fluorescent substance by which coating was carried out, melting (fuse) of the latex is carried out at an elevated temperature.
[0032] Coating containing a polysiloxane is obtained by mixing a polysiloxane directly to a fluorescent substance 4. A polysiloxane can be fused to an organic solvent and this solvent can also be made to suspend a fluorescent substance 4 after that instead. Cross linking of the polysiloxane pasted up on the particle of a fluorescent substance 4 is carried out by overheating, the catalyst, or radical initiation (radicalinitiation) after evaporation of a solvent.
[0033] In order to manufacture glass type coating from a borosilicate, a phospho silicate (phosphosilicate), or an alkali silicate, the colloidal solution of the silicate of a potassium silicate or a specific silicate is added to an ammonium hydroxide solvent. After adding a fluorescent substance 4, the mixture obtained as a result is stirred powerfully. While filtering and taking out the fluorescent substance 4 which has coating, it dries at 100 degrees C.
[0034] It is advantageous to coating that SiO2 is included [in a predetermined case] in addition to silicate. In order to manufacture such coating, the colloidal solution of a borosilicate, a phospho silicate, or an alkali silicate is added to an ammonium hydroxide solution. After adding a fluorescent substance 4, the solution of the tetraethyl orthosilicic acid salt in ethanol (tetraethyl orthosilicate) is added to mixture, and the mixture obtained as a result is stirred powerfully. The fluorescent substance 4 which has coating is dried at 100 degrees C while it is taken out.
[0035] In order to increase stability, the 2nd coating layer can be prepared. For this reason, as already explained, the colloidal solution of a borosilicate, a phospho silicate, or an alkali silicate is added to an ammonium hydroxide solution. First, the fluorescent substance 4 which already prepared coating is added to this mixture, and the solution of the tetraethyl orthosilicic acid salt in ethanol (tetraethyl orthosilicate) is added after that. After stirring powerfully, while taking out the fluorescent substance 4 which carried out duplex coating, it dries at 100 degrees C.
[0036] In order to form coating of an inorganic material, suspension including the combination of a desired coating ingredient, for example, oxide, a borate, phosphate, or these coatings ingredient is made.
[0037] It is converted into instead of by the desired particle by heat treatment after that also including the precursor of the coating ingredient according [suspension] to this invention. First, the suspension which follows, for example, contains Mg (OH)2 is prepared on the particle of a fluorescent substance 4, and is thermally converted into the layer of MgO after that.
[0038] Let especially the initiation compound used for coating containing MgO, aluminum2O3, and oxide like SiO2 be a water-soluble metal salt, a water-soluble nitrate, acetate, or citrate. One or more of the metal salts of these are underwater dissolved, while making a coating solution, and a pH value is adjusted to 7. The fluorescent substance 4 which should be covered is diffused in this solution. Thus, the aqueous suspension of the obtained fluorescent substance 4 continues contacting the ambient atmosphere which contains ammonia with scrambling until an oxide or a hydroxide precipitates to a fluorescent substance particle, while the pH value of suspension rises to 9.5. The fluorescent substance 4 which has coating is removed, and it dries. When a fluorescent substance is covered with a hydroxide, it is calcinated at the temperature which rises gradually and is converted into the oxide with which a hydroxide corresponds.
[0039] In order to cover a fluorescent substance 4 with SiO2, it prepares first suitably, the silicic acid anhydride

which can be hydrolyzed, for example, the tetraethyl orthosilicic acid, of a monomer. After adding a fluorescent substance 4, the mixture obtained as a result is stirred powerfully, and a solvent, for example, ethanol, is removed after that. The fluorescent substance 4 which has coating is exposed to the ambient atmosphere saturated with a 80-degree C steam in order to obtain coating of SiO2 of high density.

[0040] The silicic acid anhydride which can be hydrolyzed may beforehand already be condensed selectively. For this reason, it mixes in the amount of catalysts of Rarefaction HCl, and the silicic acid anhydride of a monomer is heated under reflux for 24 hours. Then, distillation removes, without including the silicic acid anhydride beforehand condensed in the solvent.

[0041] Let the initiation compound used to coating containing an orthophosphate be the fusibility metal salt which has presentation MX3 and H2O. In this case, M expresses one of Metals aluminum, Sc, Y, Lu, and La, X expresses one or more of anion CH3COO-, RO-, NO3-, Cl-, CH3COCH=C(O-) CH3, and -OOCCH2CH(OH) (COO-) CH2COO- , and y expresses the number more than zero. Generally as a solvent, water is used.

[0042] a phosphoric acid — a phosphoric acid and a urea are suitably added to this solution 85%. After filtering suitably the solution obtained as a result with a thin film nylon filter, a fluorescent substance 4 is added. It heats stirring suspension until the pH value is set to 7. After cooling to a room temperature, the fluorescent substance 4 which has coating 4 is taken out, rinsed and dried.

[0043] In order to form coating constituted from a polyphosphate, the water solution of a polyphosphate is added to the suspension of the fluorescent substance 4 which should be covered. A polyphosphate has presentation (M0.5PO3) n, and chooses M from the group of calcium, Sr, and Ba in this case, and chain length n is between 101 and 106. The water solution of the water-soluble salt of calcium, Sr, or Ba is added to this suspension. The pH value of suspension is held to an alkali field by adding ammonia or the caustic alkali solution of sodium. The fluorescent substance 4 which has coating is taken out, rinsed and dried.

[0044] In order to form coating constituted from way acid chloride, the suspension of the fluorescent substance 4 which should be covered is added to the alcoholic solution of way acid ester, and the ester is obtained from the multi-way acid (polyboric acid) which has general formula Hn-2BnO2n-1. In this case, it is n<=3. The reaction mixture obtained as a result is stirred at a room temperature for 2 to 24 hours, and the fluorescent substance 4 which has coating is taken out, and it is dried.

[0045] The example of this invention is explained to a detail below.

[0046] an example 1 — first — 30.0g (TEOS) of tetraethyl orthosilicic acid salts in 40.0ml dehydrated ethanol — 0.1M It mixes to HCl0.864ml. The reaction mixture obtained as a result is heated under reflux for 24 hours. Then, TEOS and ethanol to which condensation was not performed are removed by distillation.

[0047] SrS:Eu10g is suspended in 50.0ml of dehydrated ethanol. TEOS condensed beforehand is added to this suspension, and the mixture obtained as a result is stirred for 15 minutes. SrS:Eu which covered TEOS obtained as a result after distillation of the solvent in a vacuum is exposed to the air containing a steam with a temperature of 80 degrees C. Thickness of coating of SiO2 is set to 100nm.

[0048] A table 1 shows that quantum efficiency hardly decreases by coating of the fluorescent substance particle of SrS:Eu by the layer of SiO2 which has 100nm thickness.

[0049] Table 1: Quantum efficiency (Q. E.) of SrS:Eu which covered SiO2, and SrS:Eu, absorption (Abs.), and surface presentation [table 1]

	QE [%]	Abs. [%]	Sr [原子%]	S [原子%]	O [原子%]	Si [原子%]	C [原子%]
SrS:Eu	100	76.4	16.3	14.2	66.3	-	3.2
SiO_2-SrS:Eu	97	77.6	-	-	46.3	12.5	41.2

[0050] Next, the light emitting device 1 which has the fluorescence layer 2 containing SrS:Eu which covered the diode 3 which emits blue glow, and SiO2 is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further SrS:Eu which covered SiO2 as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.

[0051] Example 2 ammonia 250g is mixed in 750g of water, and 25g of potassium-silicate solutions of colloid (15 % of the weight) is added to this mixture. Then, SrS:Eu is added and the suspension obtained as a result is stirred powerfully. The solution of 10ml of tetraethyl orthosilicic acid salts of ethanol 750ml Naka is dropped at suspension for the period for less than 15 minutes. The reaction mixture obtained as a result is stirred for 90 minutes at a room temperature. Covered SrS:Eu is taken out and it dries at 100 degrees C. The covered fluorescent substance is again suspended in the mixture of 25g of potassium silicates on ammonia 250g in 750g of water, and colloid. 1l. of ethanol, and ethanol 500ml -- 10ml [of inner tetraethyl orthosilicic acid] mixture is dropped at this suspension. The reaction mixture obtained as a result is stirred for 60 minutes at a room temperature. SrS:Eu which has coating of a potassium silicate is taken out and it dries at 100 degrees C.

[0052] Subsequently, the light emitting device 1 which has the fluorescence layer 2 containing SrS:Eu which covered the diode 3 and the potassium silicate which emit blue glow is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. If a fluorescent substance 4 is formed on a clear layer 5, the fluorescence layer 2 containing SrS:Eu which covered the potassium silicate will be formed. Then, a light emitting device 1 is protected by the epoxy housing 6.

[0053] Example 3aluminum(NO3)3.9H2O4.45g is dissolved into 1.25l. of pure water. 85%H3PO41.37g and 36.04g of ureas are added to this solution. SrGa2 S4 is added after filtering the mixture obtained as a result in the nylon filter

of 0.2 micrometers of thickness. Suspension is stirred at 90 degrees C until the pH value of a solution is set to 7. Suspension can be cooled to a room temperature, and ejection and pure water wash fluorescent substance SrGa2 S4 which covered AlPO4 several times, and it heats at 100 degrees C for 1 hour.

[0054] Subsequently, the light emitting device 1 which has the fluorescence layer 2 containing SrGa 2O4 which covered the diode 3 and AlPO4 which emit blue glow is manufactured. For this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further SrGa2 S4 which covered AlPO4 as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.

[0055] Example 4(3.9 mols) Mg(NO3)2.6H2O1.0g is dissolved into 50ml of water. Y3aluminum 5O12 is suspended in 50ml of water, and a magnesium nitride solution is added to this suspension. The suspension which has the pH value of 7.5 and which was obtained.as a result is stirred powerfully. The pH value of suspension rises to pH9.1 with concentration ammonia liquor, consequently Mg (OH)2 begins to precipitate. After stirring powerfully for 2 hours, the fluorescent substance with which coating was performed is taken out, and it dries at 80 degrees C, and is eventually calcinated at 250 degrees C for 2 hours.

[0056] The light emitting device 1 which has the fluorescence layer 2 containing Y3aluminum 5O12 which covered the diode 3 which emits blue glow, and MgO is manufactured. For this reason, for this reason, the InGaN/AlGaN diode 3 is surrounded by the clear layer 5 of polyacrylate. A clear layer 5 contains further Y3aluminum 5O12 which covered MgO as a fluorescent substance 4. Then, a light emitting device 1 is protected by the epoxy housing 6.

[Translation done.]

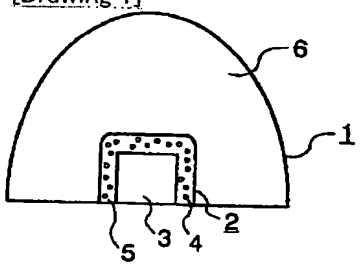
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing a light emitting device.

[Translation done.]

DRAWINGS

[Drawing 1]



[Translation done.]

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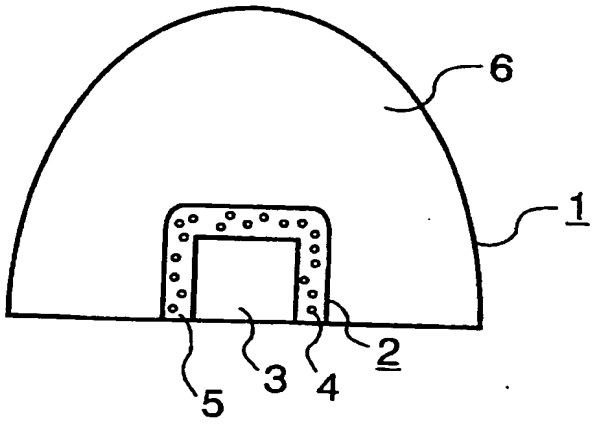
(54)【発明の名称】　発光素子

(57)【要約】
【課題】　発光素子の耐用年数の向上を図る。
【解決手段】　発光素子１は、発光ダイオード３及び蛍光層２を具える。発光素子１の耐用年数を延ばすために、蛍光層２の蛍光体４は耐水コーティングを有する。



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【特許請求の範囲】

【請求項１】　少なくとも１個の発光ダイオード及び蛍光層を設け、この蛍光体が、コーティングを有する少なくとも一つの蛍光体を具えることを特徴とする発光素子。

【請求項２】　前記コーティングを、有機材料、無機材料及びガラス材料からなる群から選択したことを特徴とする請求項１記載の発光素子。

【請求項３】　前記有機材料を、ラテックス及びポリオルガノシロキサンからなる群から選択したことを特徴とする請求項２記載の発光素子。

【請求項４】　前記ガラス材料を、ホウケイ酸塩、ホスホケイ酸塩、アルカリケイ酸塩からなる群から選択したことを特徴とする請求項２記載の発光素子。

【請求項５】　前記無機材料を、酸化物、ホウ酸塩、リン酸塩及びこれら材料の組合せからなる群から選択したことを特徴とする請求項２記載の発光素子。

【請求項６】　前記リン酸塩を、ＭをＡｌ，Ｌａ，Ｓｃ，Ｙ及びＬｕからなる群から選択したオルトリン酸塩MPO_4、又は、10^1と10^6との間の鎖長ｎ及びＭをＣａ，Ｓｒ及びＢａから選択した組成（$M_{0.5}PO_3$）を有するポリリン酸塩としたことを特徴とする請求項５記載の発光素子。

【請求項７】　前記発光体を、酸化発光体、硫化発光体、アルミン酸発光体、ホウ酸発光体、バナジン発光体及びケイ酸発光体からなる群から選択したことを特徴とする請求項１記載の発光素子。

【請求項８】　前記アルミン酸発光体を、$Y_3Al_5O_{12}$：Ｃｅ，（Ｙ，Ｇｄ）$_3$（Ａｌ，Ｇａ）$_5O_{12}$：Ｃｅ及び$BaMgAl_{10}O_{17}$：Ｅｕ，Ｍｎからなる群から選択したことを特徴とする請求項７記載の発光素子。

【請求項９】　前記硫化発光体を、ＳｒＳ：Ｅｕ，$SrGa_2S_4$：Ｅｕ，（Ｓｒ，Ｃａ，Ｂａ）（Ａｌ，Ｇａ）$_2S_4$：Ｅｕ，SrY_2S_4：Ｅｕ，（Ｍｇ，Ｃａ）Ｓ：Ｅｕ，ＳｒＳ：Ｃｅ，ＣａＳ：Ｃｅ，$CaLa_2S_4$：Ｃｅ及びＣａＳ：Ｃｅ，Ｅｕからなる群から選択したことを特徴とする請求項７記載の発光素子。

【請求項１０】　前記発光素子が、SiO_2及びケイ酸塩のコーティングを有するＳｒＳ：Ｅｕを含むことを特徴とする請求項１から９のうちのいずれか１項に記載の発光素子。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、少なくとも１個の発光ダイオード及び蛍光層を設けた発光素子に関するものである。

【０００２】

【従来の技術】固体光源、例えば発光ダイオード、特に半導体ダイオードが従来既知である。半導体ダイオード

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の発光は、順方向にバイアスをかけられた半導体のｐｎ遷移の遷移領域の電子－ホール対（励起子）の再結合に基づく。半導体のバンドギャップの寸法は、放出された光の波長を大まかに決定する。

【０００３】可視光を放射する半導体ダイオードは、カラーディスプレイでも使用される。カラーディスプレイにおいて、３原色の赤色、緑色及び青色を、赤色発光半導体ダイオード、緑色発光半導体ダイオード及び青色発光半導体ダイオードのアレイによって発生させる。しかしながら、この場合、本物に近いカラー画像描写、特に画像中の緑色及び青色の真の描写を達成する方法が問題となる。

【０００４】ＵＶ放射を行う半導体ダイオードの開発によって、ダイオードのアドレス指定を行うカラー画像スクリーン上における真のカラー画像表示の可能性が増大している。ＵＶ放射を行う半導体ダイオードとＵＶ放射を可視光に変換する発光体を組み合わせることによって、半導体ダイオードによる所望の可視光のうちの任意の色及び白色を表現することができる。そのようなカラーディスプレイは、例えばドイツ国特許番号第１９８００９８３号から既知である。この原理は、適切な発光体を使用する場合には、紫色又は青色光を出射する半導体ダイオードにも当てはまる。

【０００５】

【発明が解決しようとする課題】従来のランプと比較した場合における発光半導体ダイオードの主な利点は、高い安定性及びそれに伴う長い耐用年数である。ダイオードのアドレス指定を行うカラー画像スクリーンの制限要因は、蛍光層で用いられる蛍光体の安定性である。蛍光体が周辺雰囲気から完全に分離されないので、水に反応する蛍光体は、空気からの水分によって加水分解されるおそれがある。比較的安定な蛍光体も、高温及び高湿度の影響下で加水分解されるおそれがある。蛍光層中の蛍光体の劣化によって、発光素子の耐用年数が短縮する。

【０００６】本発明の目的は、発光ダイオード及び蛍光層が設けられた耐用年数が向上した発光素子を提供することである。

【０００７】

【課題を解決するための手段】この目的は、少なくとも１個の発光ダイオード及び蛍光層を設け、この蛍光体が、コーティングを有する少なくとも一つの蛍光体を具えることを特徴とする発光素子によって達成される。

【０００８】空気中の水分によって生じる劣化は、高密度の耐水フィルムを有する蛍光体粒子のコーティングによって防止される。

【０００９】好適には、前記コーティングを、有機材料、無機材料及びガラス材料からなる群から選択する。

【００１０】更に好適には、前記有機材料を、ラテックス及びポリオルガノシロキサンからなる群から選択する。

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【００１１】更に好適には、前記ガラス材料を、ホウケイ酸塩、ホスホケイ酸塩、アルカリケイ酸塩からなる群から選択する。

【００１２】更に好適には、前記無機材料を、酸化物、ホウ酸塩、リン酸塩及びこれら材料の組合せからなる群から選択する。

【００１３】これら有機材料、ガラス材料及び無機材料は、蛍光体粒子に対して肉薄で水に対して不溶性のコーティングを形成し、そのコーティングは蛍光体と反応せず、かつ、ＵＶ放射すなわち４１０－４５０ｎｍの波長を有する放射によって劣化されない。さらに、コーティングは無色であり、したがって、蛍光体の色の値に影響を及ぼさない。

【００１４】好適例は、前記リン酸塩を、ＭをＡｌ，Ｌａ，Ｓｃ，Ｙ及びＬｕからなる群から選択したオルトリン酸塩MPO_4、又は、10^1と10^6との間の鎖長ｎ及びＭをＣａ，Ｓｒ及びＢａから選択した組成（$M_{0.5}PO_3$）を有するポリリン酸塩としたことを特徴とする。

【００１５】これらリン酸塩は、蛍光体上に高密度の表面を有する十分に閉ざされた薄膜を形成する。

【００１６】好適には、前記発光体を、酸化発光体、硫化発光体、アルミン酸発光体、ホウ酸発光体、バナジン発光体及びケイ酸発光体からなる群から選択する。

【００１７】これら発光体を適切な活性剤と組み合わせることによって、ＵＶ放射又は青色光を、更に長い波長の可視光に変換する。

【００１８】好適には、前記アルミン酸発光体を、$Y_3Al_5O_{12}:Ce$，$(Y,Gd)_3(Al,Ga)_5O_{12}:Ce$及び$BaMgAl_{10}O_{17}:Eu,Mn$からなる群から選択する。

【００１９】特に、特別なコーティングを有する$Y_3Al_5O_{12}$は、青色光によって励起されると黄色を発する蛍光体となる。

【００２０】更に好適には、前記硫化発光体を、ＳｒＳ：Ｅｕ，$SrGa_2S_4:Eu$，$(Sr,Ca,Ba)(Al,Ga)_2S_4:Eu$，$SrY_2S_4:Eu$，$(Mg,Ca)S:Eu$，ＳｒＳ：Ｃｅ，ＣａＳ：Ｃｅ，$CaLa_2S_4:Ce$及びＣａＳ：Ｃｅ，Ｅｕからなる群から選択する。

【００２１】特に、ＳｒＳ：Ｅｕのような硫化物を含む蛍光体は、以下の反応式に基づいて空気中の水分によって加水分解される。

$SrS+2H_2O \rightarrow Sr(OH)_2+H_2S$

したがって、好適には硫化物を有するコーティングによって蛍光体が安定化される。

【００２２】更に好適には、前記発光素子が、SiO_2及びケイ酸塩のコーティングを有するＳｒＳ：Ｅｕを含む。

【００２３】

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【発明の実施の形態】図１に示すように、発光素子１は、最も簡単な場合において、ＵＶ放射又は青色光を発するダイオード２と、ダイオード３に設けられた蛍光層２とを具える。本実施の形態では、蛍光層２は、耐水コーティングを行った蛍光体４を有する透明層５を具える。透明層５の材料を、例えば、ポリアクリレート(polyacrylate)、ポリスチロール(polystyrol)、エポキシ樹脂(epoxide resin)、ポリプロピレン、ポリカーボネート又は他の一部の重合体とすることができる。

【００２４】大量生産される製品のような発光素子１は、通常、エポキシ樹脂のレンズが成形されるエポキシハウジング６によって保護される。このレンズは、発光素子１からの光の案内を向上させる役割を果たす。本実施の形態では、蛍光層２を透明層５とエポキシハウジング６との間に設けてもよい。蛍光層２を、エポキシハウジング６の外側のコーティングとして設けることもできる。これらの場合において、蛍光層２は、コーティングを設けた蛍光体４を具える蛍光体混合物(phosphor)を含む。他の実施の形態では、蛍光層２がエポキシ樹脂から形成され、蛍光体４にコーティングを設ける。本実施の形態では、蛍光層２はエポキシハウジング６を形成する。

【００２５】発光素子が例えば白色光を出射すべき場合、蛍光層は、赤色を発する蛍光体、青色を発する蛍光体及び緑色を発する蛍光体の物理的な混合を含む。

【００２６】大型の２次元ディスプレイを、発光ダイオード３のアレイによって容易に製造することができる。そのような発光ダイオード３のアレイを、蛍光層２によって押しつけられたガラスプレートによってカバーすることができる。蛍光層２は、三角形に配置した３点パターンで設けられた赤色発光体、緑色発光体及び青色発光体を具える。

【００２７】ＵＶを出射するダイオード３は、例えば、ＩＮＧａＮ又はＧａＮを含む。このＵＶを出射するダイオード３は、半値幅ＦＷＨＭ＜５０ｎｍである３７０ｎｍと４１０ｎｍの間の最大発光(emission maximun)を有する。４１０ｎｍと４５０ｎｍの間の波長を有する青色光を出射するダイオード３は、例えば、ＩｎＧａＮ／ＡｌＧａＮ構造を有する。ＵＶ又は青色光を出射するダイオード３に電気的なエネルギーを供給する手段を、発光を維持するために設ける。その手段は、少なくとも２個の電極を有する。

【００２８】蛍光層２で使用される蛍光体を、例えば、酸化蛍光体、硫化蛍光体、アルミン酸蛍光体、ほう酸蛍光体、バナジン酸蛍光体又は珪酸蛍光体とする。特に、以下の蛍光体が使用される：$Y_3Al_5O_{12}:Ce$，$(Y,Gd)_3(Al,Ga)_5O_{12}:Ce$，$BaMgAl_{10}O_{17}:Eu,Mn$，$Y_2O_2S:Eu,Bi$，$YVO_4:Eu,Bi$，$YVO_4:Eu,Bi$，$YBO_3:Ce,Tb$，$(Sr,Ba)_2SiO_4:E$

u，$Ca_2MgSi_2O_7$：Eu，Sr_2CeO_4：Eu，SrS：Eu，$SrGa_2S_4$：Eu，（Sr，Ca，Ba）（Al，Ga）$_2S_4$：Eu，SrY_2S_4：Eu，（Ca，Sr）S：Eu，（Mg，Ca）S：Eu，SrS：Ce，CaS：Ce，$CaLa_2S_4$：Ce又はCaS：Ce，Eu。

【００２９】蛍光体４の粒子は、肉薄で平坦な耐水層によって被覆される。対数コーティングの層の厚さは、通常、０．００１－０．２μｍであり、したがって、非常に薄いので、光子が、エネルギーをほとんど損失することなく層を通過することができる。

【００３０】コーティングの形成は、コーティング材料に応じて種々の方法に従う。

【００３１】蛍光体をラテックスで被覆するために、ラテックスを有機溶媒で溶解する。その後、蛍光体４がこの溶媒中で懸濁(suspend)される。ラテックスは、ラテックスが溶解しない溶媒を加えることによって、蛍光体２の粒子に沈殿(precipitate)される。コーティングされた蛍光体を濾過及び乾燥した後、ラテックスは高温で溶融(fuse)される。

【００３２】ポリシロキサンを含むコーティングは、ポリシロキサンを蛍光体４に直接混合することによって得られる。代わりに、ポリシロキサンを有機溶媒に溶融し、その後、蛍光体４をこの溶媒に懸濁させることもできる。溶媒の蒸発後、蛍光体４の粒子に接着するポリシロキサンを、過熱、触媒又はラディカルな開始(radical initiation)によって交差結合させる。

【００３３】ホウケイ酸塩、ホスホケイ酸塩(phosphosilicate)又はアルカリケイ酸塩からガラスタイプのコーティングを製造するために、例えば珪酸カリウム又は珪酸ナトリウムの珪酸塩のコロイド溶液を、水酸化アンモニウム溶媒に加える。蛍光体４を加えた後、結果的に得られる混合物を強力にかき混ぜる。コーティングを有する蛍光体４を濾過して取り出すとともに、１００℃で乾燥する。

【００３４】所定の場合には、珪酸塩に加えてSiO_2を含むのがコーティングに有利である。そのようなコーティングを製造するためには、ホウケイ酸塩、ホスホケイ酸塩又はアルカリケイ酸塩のコロイド溶液を水酸化アンモニウム溶液に加える。蛍光体４を加えた後、エタノール中のテトラエチルオルトケイ酸塩(tetraethyl orthosilicate)の溶液を混合物に加え、結果的に得られた混合物を強力にかき混ぜる。コーティングを有する蛍光体４は、取り出されるとともに１００℃で乾燥される。

【００３５】安定性を増大させるために、第２のコーティング層を設けることができる。このために、既に説明したように、ホウケイ酸塩、ホスホケイ酸塩又はアルカリケイ酸塩のコロイド溶液を水酸化アンモニウム溶液に加える。先ず、既にコーティングを設けた蛍光体４をこの混合物に加え、その後、エタノール中のテトラエチルオルトケイ酸塩(tetraethyl orthosilicate)の溶液を加える。強力にかき混ぜた後、二重コーティングした蛍光体４を取り出すとともに１００℃で乾燥する。

【００３６】無機材料のコーティングを形成するために、所望のコーティング材料、例えば、酸化物、ホウ酸塩、リン酸塩又はこれらコーティング材料の組合せを含む懸濁液を作る。

【００３７】代わりに、懸濁液は、本発明によるコーティング材料の前駆物質も含み、それは、その後、熱処理によって所望の粒子に転化される。したがって、例えば、Mg（OH）$_2$を含む懸濁液は、先ず、蛍光体４の粒子の上に設けられ、その後、MgOの層に熱的に転化される。

【００３８】MgO，Al_2O_3，SiO_2のような酸化物を含むコーティングに使用される開始化合物を、水溶性の金属塩、特に、水溶性の硝酸塩、酢酸塩、又はクエン酸塩とする。これら金属塩の一つ以上が、コーティング溶液を作る間に水中で溶解され、ｐＨ値が７に調整される。被覆すべき蛍光体４はこの溶液中で拡散する。このようにして得られた蛍光体４の水性懸濁液は、懸濁液のｐＨ値が９．５まで上昇するとともに酸化物又は水酸化物が蛍光体粒子に沈殿するまで、かき混ぜながらアンモニアを含む雰囲気に接触し続ける。コーティングを有する蛍光体４が取り除かれ及び乾燥される。蛍光体が水酸化物で被覆された場合、それは、段階的に上昇する温度で焼成されて、水酸化物が、対応する酸化物に転化される。

【００３９】蛍光体４をSiO_2で被覆するために、好適には、単量体の加水分解可能な無水ケイ酸、例えば、テトラエチルオルトケイ酸を最初に調合する。蛍光体４を加えた後、結果的に得られる混合物を強力にかき混ぜ、その後、溶媒、例えばエタノールを除去する。コーティングを有する蛍光体４は、高密度のSiO_2のコーティングを得るために８０℃の水蒸気で飽和した雰囲気に露出する。

【００４０】加水分解可能な無水ケイ酸を予め既に部分的に凝縮してもよい。このために、単量体の無水ケイ酸を、希薄ＨＣｌの触媒量に混合し、還流下で２４時間加熱する。その後、溶媒を、予め凝縮された無水ケイ酸を含むことなく、蒸留によって除去する。

【００４１】正リン酸塩を含むコーティングに対して用いられる開始化合物を、組成$MX_3 \cdot H_2O$を有する可溶性金属塩とする。この場合、Mは、金属Ａｌ，Ｓｃ，Ｙ，Ｌｕ及びＬａのうちの一つを表し、Xは、陰イオンCH_3COO^-，RO^-，NO_3^-，Cl^-，$CH_3COCH{=}C(O^-)CH_3$及び$^-OOCCH_2CH(OH)(COO^-)CH_2COO^-$のうちの一つ以上を表し、ｙは、零以上の数を表す。溶媒としては一般に水が用いられる。

【００４２】リン酸、好適には８５％リン酸及び尿素を

この溶液に加える。結果的に得られる溶液を好適には薄膜ナイロンフィルタによって濾過した後、蛍光体４を加える。懸濁液を、そのｐＨ値が７になるまでかき混ぜながら加熱する。室温まで冷却した後、コーティング４を有する蛍光体４は、取り出され、すすがれ、かつ、乾燥される。

【００４３】ポリリン酸塩から構成したコーティングを形成するために、ポリリン酸塩の水溶液を、被覆すべき蛍光体４の懸濁液に加える。ポリリン酸塩は、組成（$M_{0.5}PO_3$）$_n$を有し、この場合、Mを、Ｃａ，Ｓｒ及びＢａの群から選択し、鎖長ｎは10^1と10^6の間にある。Ｃａ，Ｓｒ又はＢａの水溶性の塩の水溶液を、この懸濁液に加える。懸濁液のｐＨ値は、アンモニア又はナトリウムの苛性アルカリ溶液を加えることによって、アルカリ領域に保持される。コーティングを有する蛍光体４は、取り出され、すすがれ、かつ、乾燥される。

【００４４】ほう酸塩から構成したコーティングを形成するために、ほう酸エステルのアルコール溶液に、被覆すべき蛍光体４の懸濁液を加え、そのエステルは、一般式$H_{n-2}B_nO_{2n-1}$を有する多ほう酸(polyboric acid)から得られる。この場合、ｎ≦３である。結果的に得られる反応混合物は、２－２４時間室温でかき混ぜられ、コーティングを有する蛍光体４が取り出され、かつ、乾燥される。

【００４５】本発明の実施例を、以下で詳細に説明する。

【００４６】実施例１

先ず、４０．０ｍｌ無水エタノール中のテトラエチルオルトケイ酸塩（ＴＥＯＳ）３０．０ｇを、０．１Ｍ ＨＣｌ０．８６４ｍｌに混合する。結果的に得られる反応混合物は、還流下で２４時間加熱される。その後、凝縮が行われなかったＴＥＯＳ及びエタノールが、蒸留によって除去される。

【００４７】ＳｒＳ：Ｅｕ１０ｇを、無水エタノール５０．０ｍｌで懸濁する。予め凝縮されたＴＥＯＳをこの懸濁に加え、結果的に得られる混合物を１５分間かき混ぜる。真空における溶媒の蒸留後、結果的に得られるＴＥＯＳを被覆したＳｒＳ：Ｅｕを、８０℃の温度の水蒸気を含む空気に露出する。SiO_2のコーティングの膜厚を１００ｎｍとする。

【００４８】表１は、１００ｎｍの膜厚を有するSiO_2の層によるＳｒＳ：Ｅｕの蛍光体粒子のコーティングによって量子効率がほとんど減少しないことを示す。

【００４９】表１：SiO_2を被覆したＳｒＳ：Ｅｕ及びＳｒＳ：Ｅｕの量子効率（Ｑ．Ｅ．）、吸収（Ａｂｓ．）及び表面組成

【表１】

	QE [%]	Abs. [%]	Sr [原子%]	S [原子%]	O [原子%]	Si [原子%]	C [原子%]
SrS:Eu	100	76.4	16.3	14.2	66.3	-	3.2
SiO_2-SrS:Eu	97	77.6	-	-	46.3	12.5	41.2

【００５０】次に、青色光を発するダイオード３及びSiO_2を被覆したＳｒＳ：Ｅｕを含む蛍光層２を有する発光素子１を製造する。このために、ＩｎＧａＮ／ＡｌＧａＮダイオード３を、ポリアクリレートの透明層５によって包囲する。透明層５は、蛍光体４としてのSiO_2を被覆したＳｒＳ：Ｅｕを更に含む。その後、発光素子１はエポキシハウジング６によって保護される。

【００５１】実施例２

アンモニア２５０ｇを水７５０ｇに混合し、（１５重量％の）コロイド状のケイ酸カリウム溶液２５ｇをこの混合物に加える。その後、ＳｒＳ：Ｅｕを加え、結果的に得られる懸濁液を強力にかき混ぜる。エタノール７５０ｍｌ中のテトラエチルオルトケイ酸塩１０ｍｌの溶液を、１５分未満の期間に亘って懸濁液に滴下する。結果的に得られる反応混合物は、室温で９０分間かき混ぜられる。被覆されたＳｒＳ：Ｅｕが取り出され、１００℃で乾燥される。被覆された蛍光体は、水７５０ｇ中のアンモニア２５０ｇ及びコロイド上のケイ酸カリウム２５ｇの混合物中で再び懸濁される。エタノール１リットルと、エタノール５００ｍｌ中のテトラエチルオルトケイ酸１０ｍｌとの混合物を、この懸濁液に滴下する。結果的に得られる反応混合物を、室温で６０分間かき混ぜる。ケイ酸カリウムのコーティングを有するＳｒＳ：Ｅｕが取り出され、１００℃で乾燥される。

【００５２】次いで、青色光を発するダイオード３及びケイ酸カリウムを被覆したＳｒＳ：Ｅｕを含む蛍光層２を有する発光素子１を製造する。このために、ＩｎＧａＮ／ＡｌＧａＮダイオード３は、ポリアクリレートの透明層５によって包囲される。蛍光体４が透明層５の上に設けられると、ケイ酸カリウムを被覆したＳｒＳ：Ｅｕを含む蛍光層２が設けられる。その後、発光素子１は、エポキシハウジング６によって保護される。

【００５３】実施例３

$Al(NO_3)_3 \cdot 9H_2O$ ４．４５ｇを、純水１．２５リットル中に溶解する。８５％H_3PO_4 １．３７ｇ及び尿素３６．０４ｇをこの溶液に加える。結果的に得られる混合物を膜厚０．２μｍのナイロンフィルタに濾過した後、$SrGa_2S_4$を加える。懸濁液を、溶液のｐＨ値が７になるまで９０℃でかき混ぜる。懸濁液を室温まで冷却することができ、$AlPO_4$を被覆した蛍光体$SrGa_2S_4$を取り出し、純水で数回洗浄し、かつ、１００℃で１時間加熱する。

【００５４】次いで、青色光を発するダイオード３及び$AlPO_4$を被覆した$SrGa_2O_4$を含む蛍光層２を

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有する発光素子１を製造する。このために、ＩｎＧａＮ／ＡｌＧａＮダイオード３を、ポリアクリレートの透明層５によって包囲する。透明層５は、蛍光体４としての$AlPO_4$を被覆した$SrGa_2S_4$を更に含む。その後、発光素子１はエポキシハウジング６によって保護される。

【００５５】実施例４

（３．９モルの）$Mg(NO_3)_2 \cdot 6H_2O$１．０ｇを、水５０ｍｌ中に溶解する。$Y_3Al_5O_{12}$を水５０ｍｌ中で懸濁し、窒化マグネシウム溶液をこの懸濁液に加える。７．５のｐＨ値を有する結果的に得られた懸濁液を強力にかき混ぜる。懸濁液のｐＨ値は、濃縮アンモニア溶液によってｐＨ９．１まで上昇し、その結果、$Mg(OH)_2$が沈殿し始める。強力に２時間かき混ぜた後、コーティングが施された蛍光体が取り出され、８０℃で乾燥され、最終的には２５０℃で２時間焼成される。

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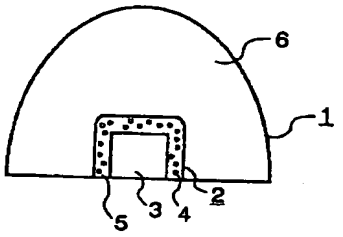
【００５６】青色光を発するダイオード３及びＭｇＯを被覆した$Y_3Al_5O_{12}$を含む蛍光層２を有する発光素子１を製造する。このために、このために、ＩｎＧａＮ／ＡｌＧａＮダイオード３を、ポリアクリレートの透明層５によって包囲する。透明層５は、蛍光体４としてのＭｇＯを被覆した$Y_3Al_5O_{12}$を更に含む。その後、発光素子１はエポキシハウジング６によって保護される。

【図面の簡単な説明】

【図１】　発光素子を示す図である。

【図１】



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